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## Antihydrophobic Cosolvent Effects for Alkylation Reactions in Water Solution, Particularly Oxygen versus Carbon Alkylations of Phenoxide Ions.

Breslow R, Groves K, Mayer MU.

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027.

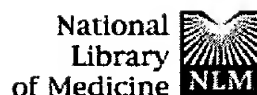
Antihydrophobic cosolvents such as ethanol increase the solubility of hydrophobic molecules in water, and they also affect the rates of reactions involving hydrophobic surfaces. In simple reactions of hydrocarbons, such as the Diels-Alder dimerization of 1,3-cyclopentadiene, the rate and solubility data directly reflect the geometry of the transition state, in which some hydrophobic surface becomes hidden. In reactions involving polar groups, such as alkylations of phenoxide ions or S(N)1 ionizations of alkyl halides, cosolvents in water can have other effects as well. However, solvation of hydrophobic surfaces is still important. By the use of structure-reactivity relationships, and comparing the effects of ethanol and DMSO as solvents, it has been possible to sort out these effects. The conclusions are reinforced by an ab initio computer model for hydrophobic solvation. The result is a sensible transition state for phenoxide ion as a nucleophile, using its oxygen n electrons to avoid loss of conjugation. The geometry of alkylation of aniline is very different, involving packing (stacking) of the aniline ring onto the phenyl ring of a benzyl group in the benzylation reaction. The alkylation of phenoxide ions by benzylic chlorides can occur both at the phenoxide oxygen and on ortho and para positions of the ring. Carbon alkylation occurs in water, but not in nonpolar organic solvents, and it is observed only when the phenoxide has at least one methyl substituent ortho, meta, or para. The effects of phenol substituents and of antihydrophobic cosolvents on the rates of the competing alkylation processes indicate that in water the carbon alkylation involves a transition state with hydrophobic packing of the benzyl group onto the phenol ring. The results also support our conclusion that oxygen alkylation uses the n electrons of the phenoxide oxygen as the nucleophile and does not have hydrophobic overlap in the transition state. The mechanisms and explanations for competing oxygen and carbon alkylations differ from previous proposals by others.

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## A contribution to the debate about hydrophobic effects.

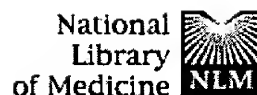
**Hvidt A.**

Based on available measurements of the concentration dependence of the volume and the heat capacity of aqueous solutions of low molecular weight compounds it is suggested that non-polar molecules or non-polar groups in aqueous solution fluctuate between solvated and non-solvated states. The experimental data indicate that the change in standard free energy of the hydrophobic solvation is positive and so large that the solvation is incomplete even in the most dilute solutions studied. It is tentatively suggested that the hydrophobic solvation enhances the solubility in water of non-polar substances, and that the reason why non-polar groups in protein solutions are buried in the interior of the protein conformations is a low degree of solvation of these groups in the solvent exposed state.

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## Formulation of a reservoir-type testosterone transdermal delivery system.

Kim MK, Zhao H, Lee CH, Kim DD.

College of Pharmacy, Pusan National University, 609-735, Pusan, South Korea.

A reservoir-type transdermal delivery system of testosterone (TS) was developed using an ethanol/water (70:30) cosolvent system as the vehicle. The maximum permeation rate achieved by 70% (v/v) of ethanol was further increased from 2.69 to 47.83 microg/cm(2)/h with the addition of 1.0% dodecylamine as the skin permeation enhancer. The permeation rate of TS through the ethylene vinyl acetate (EVA) membrane was observed to increase as the vinyl acetate content in the copolymer increased. Addition of 1.0% (w/w) gelling agent, hydroxypropyl methylcellulose (HPMC), in the reservoir formulation resulted in desirable rheological properties with an insignificant effect on the skin permeation rate of TS. Thus, a new transdermal delivery system for TS was formulated using EVA membrane coated with a pressure-sensitive adhesive (Duro-Tak 87-2510) and HPMC as a gelling agent. This experimental patch showed comparable plasma concentration profiles in the in vivo study when compared with a commercial product, Androderm(R). Moreover, the results suggested the possibility of further enhancing the permeation rate of TS by controlling the composition of the reservoir formulation.

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